

## Ti-phlogopites of the Shaw's Cove minette: a comparison with micas of other lamprophyres, potassic rocks, kimberlites, and mantle xenoliths

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### Abstract

The two generations of micas in the Shaw's Cove minette (mica–potash feldspar lamprophyre) of northern New Brunswick, Canada, are TiO<sub>2</sub>-rich phlogopites with variable but low silica and potash contents, low soda, and effectively all their aluminum in tetrahedral sites. A majority of the micas have an excess of Y cations and a deficiency of X cations; there are positive correlations between excess Y ions and number of Al ions in Z sites, between K<sub>2</sub>O and SiO<sub>2</sub> contents, and between K<sub>2</sub>O and volatile-free totals; yet the micas optically appear fresh, do not respond to hydration or glycolation, and X-ray diffraction patterns show none of the peaks of talc, montmorillonites, vermiculite, or 7- or 14-Å chlorites. This suggests that some normally octahedrally coordinated cations and water or hydronium ions are located in the interlayer X sites. Phenocryst micas are sharply zoned. Cores are paler colored and have high *mg* [atomic ratio Mg/(Mg + Fe<sup>2+</sup>)] (0.81–0.88), Cr<sub>2</sub>O<sub>3</sub> ( $\bar{x}$  = 0.88 wt.%), and NiO ( $\bar{x}$  = 0.08 wt.%), but relatively low TiO<sub>2</sub> ( $\bar{x}$  = 2.93 wt.%), and negligible BaO. Phenocryst rims and groundmass micas are darker reddish brown and have lower *mg* (0.68–0.79), nil Cr<sub>2</sub>O<sub>3</sub> and NiO, but high TiO<sub>2</sub> ( $\bar{x}$  = 5.40 wt.%) and BaO ( $\bar{x}$  = 0.38 wt.%). Micas in minettes from other localities (62 analyses) are frequently richer in silica and potash than the Shaw's Cove samples but otherwise are generally chemically comparable. Chemical zoning or bimodalism is nearly universal in minette micas, though the boundary between high-*mg*–low-TiO<sub>2</sub> (phenocryst) and low-*mg*–high-TiO<sub>2</sub> (groundmass) groups varies from province to province and even from minette to minette within a swarm.

Comparison of analyses of minette micas with 353 analyses of micas from other mafic (largely potassic) rocks indicates that micas chemically indistinguishable from those of minettes can be found within some other lamprophyres, (ultra)potassic rocks, kimberlites, and high-pressure xenoliths in alkaline volcanic rocks and kimberlites, though each of these groups also contains micas unlike those in minettes. Those kimberlite phlogopites that match minette micas are predominantly secondary rims of phenocrysts (or megacrysts) or groundmass crystals (mainly "Type II"), but some are unzoned pre-fluidization phenocrysts. While primary, primary-metasomatic, and MARID-suite phlogopites of mantle xenoliths are unlike minette micas (higher *mg* and SiO<sub>2</sub>, lower TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>), some of the secondary-metasomatic phlogopites in sheared garnetiferous mantle xenoliths are wholly minette-like.

The chemical identity of minette-mica phenocryst cores and some phenocrysts of diverse mantle-derived rocks implies crystallization under similar conditions. By analogy with the chemistry of phlogopites produced experimentally in potassic systems at high pressures and studies of equilibration conditions of natural phlogopites, it is concluded that phenocrystic phlogopites in minettes may form at temperatures and pressures up to at least ~1250°C and ~40 kbar and probably under *f*<sub>O<sub>2</sub></sub> conditions between the NNO and HM buffers: higher *f*<sub>O<sub>2</sub></sub> than for primary, primary-metasomatic, and MARID-suite micas in kimberlites and their included xenoliths.

### Introduction

Magnesium-rich trioctahedral micas are critical phases in most lamprophyres but especially in minettes (biotite–

K-feldspar lamprophyres) and kersantites (biotite–plagioclase lamprophyres) in which they are the dominant ferromagnesian mineral. Studies of the mineral chemistry of lamprophyres are relatively few in number; this undoubtedly contributes to the present lack of agreement on their petrogenesis. If minettes are in fact mantle-derived

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(Bachinski and Scott, 1979, 1980), then detailed examination of the chemistry of their micas plus a comparison with the micas of other potassic mantle-derived rocks may yield useful information relating to the distribution and movement of water and large lithophile ions in the subcontinental upper mantle as well as the chemical and/or genetic relationships, if any, between minette magma and other potassic magmas.

Micas of minettes and other lamprophyres are nearly universally zoned discontinuously (see, *e.g.*, Velde, 1969): phenocrysts have lighter-colored cores surrounded by darker rims generally equivalent in color to the groundmass micas. Métais *et al.* (1962) were the first to confirm that this color zonation is indeed due to differing chemical composition. They semi-quantitatively demonstrated that in the micas of a minette (and a kersantite) the paler cores are richer in magnesium and chromium and are poorer in iron, titanium, manganese, barium, and cerium than the darker rims. Similar zoning has since been observed in the micas of ultrapotassic rocks and lamproites (*e.g.*, Carmichael, 1967; Nicholls, 1969; Velde, 1969, 1975; Mitchell, 1981), carbonatites (*e.g.*, Heinrich, 1966; Rimsaite, 1969; Gaspar and Wyllie, 1982), kimberlites (*e.g.*, Emeleus and Andrews, 1975; Boettcher *et al.*, 1977, 1979; Smith *et al.*, 1978; Mitchell and Meyer, 1980; Boctor and Boyd, 1982), and ultramafic mantle xenoliths in both basaltic rocks (*e.g.*, Dawson *et al.*, 1970) and kimberlites (*e.g.*, Boettcher *et al.*, 1977, 1979; Rawlinson and Dawson, 1979; Jones *et al.*, 1982).

### Phlogopites of the Shaw's Cove minette

A 15-meter-thick minette sill crops out on the southern shore of the Restigouche River at Shaw's Cove, west of the town of Dalhousie, in northernmost New Brunswick, Canada, where it has been emplaced along a conglomerate-sandstone bedding plane of the lowermost Middle Devonian Campbellton Formation. On stratigraphic grounds the minette is presumed to be no younger than Late Devonian in age. Within the minette, phenocrysts of phlogopite, diopsidic clinopyroxene, and yellowish-green phyllosilicate pseudomorphs after olivine occur in a groundmass composed of a second generation of phlogopite and clinopyroxene poikilitically enclosed by crystals of sanidine. Accessory phases include apatite, titanomagnetite, sphene, and analcime.

Phenocrystic phlogopites of the Shaw's Cove minette have pale reddish brown cores surrounded by darker rims. The core boundaries are frequently resorbed in a manner similar to that described by Mitchell and Meyer (1980). The rims correspond in color and other optical properties to the smaller phlogopites in the groundmass, both of which show normal absorption. Fifty-one micas from eight samples from a section through the minette were analyzed (by E. L. Simpson) using the Cambridge Mark V electron microprobe and Ortech energy-dispersive system of the Department of Geology, Dalhousie University. The accelerating voltage was 15 kV, beam

current was 5 nanoamps., spot size was as small as possible (generally about 1 or 1.5 microns), resolution was 159 eV, and the software package EDATA (Smith and Gold, 1976) was employed. Standards were those of Dalhousie University: BIO LP6, KK (a kaersutite), natural sanidine and albite, Will (a willemite), o1 174.1, Cr metal, Ni metal, Ilm 96189, and Opx R62.

Representative analyses of these titaniferous phlogopites ("titanphlogopites" in the terminology recommended by Rock, 1982) are presented in Table 1a. All the micas are trioctahedral and have *mg* (= atomic ratio  $Mg/(Mg + Fe^{+2})$ ) values equal to or greater than 0.68, high titania, low silica, and moderate alumina. Structural formulae calculated on the basis of 22 oxygens (Simpson, 1980) show that the number of Si ions ranges from 4.824 to 5.624 and Al from 2.999 to 2.987 per formula unit. Aluminum is essentially confined to tetrahedrally coordinated, or Z, sites: only three of the 51 micas contain any octahedrally coordinated Al. As Si + Al is less than 8.000 for nearly all the micas, the Z sites must be completed by either titanium or ferric iron. Since the Shaw's Cove minette contains important amounts of  $Fe_2O_3$  (Simpson, 1980), it is possible that its micas have a "tetraferriphlogopite" component. However, ferric iron in the Z sites of phlogopites is believed to produce reverse pleochroism (Hogarth *et al.*, 1970; Farmer and Boettcher, 1981) which we did not observe; also, tetraferriphlogopites have only been reported from rocks with very low alumina contents (*e.g.*, Wendlandt, 1977), much lower than those of minettes. Farmer and Boettcher (1981) have suggested that the sequence of tetrahedral site preference in phlogopites is  $Si > Al > Ti > Fe^{+3}$ , since all normal phlogopites have Si + Al + Ti greater than 8 while all known reverse phlogopites have this sum less than 8. The Shaw's Cove micas all have Si + Al + Ti greater than 8. We therefore conclude that Ti rather than  $Fe^{+3}$  occupies the tetrahedral sites unfilled by Si and Al.

The range of values for any given oxide in the mica analyses is relatively broad but similar to literature values for micas in other minettes (see below). Several points concerning the data, however, warrant special comment.

### TiO<sub>2</sub>, *mg*, and trace elements

The analytical results for TiO<sub>2</sub>, MgO, FeO, and the trace elements in the micas are markedly bimodal (Table 1b and Figure 1a,b,c.). A plot of wt.% TiO<sub>2</sub> against *mg* defines two chemically distinct groups of micas: Group 1, with high *mg*, low TiO<sub>2</sub>, and significant concentrations of Cr and Ni but negligible Ba, and Group 2, with low *mg*, high TiO<sub>2</sub>, no Cr or Ni but important amounts of Ba. The micas of Group 2, in fact, are the major carrier of Ba in the minette as the maximum amount of BaO in the feldspar is 0.20 wt.% (Simpson, 1980).

With few exceptions, light-colored phenocryst cores comprise Group 1, darker phenocryst rims and groundmass crystals Group 2. (We did not detect any reversely zoned micas as are occasionally seen in minettes else-

Table 1a. Representative analyses of phlogopites from the Shaw's Cove minette (oxides in wt.%)

	SC25c-9	SC25c-10	SC26-1	SC26-5	SC26-13	SC27b-1	SC27b-12a	SC30-11	SC30-17
Type*	PR	MC	G	G	G	G	G	PR	G
SiO <sub>2</sub>	35.18	38.32	32.13	33.88	35.11	34.30	36.69	34.89	36.19
TiO <sub>2</sub>	4.82	3.18	6.39	4.90	5.00	5.01	5.55	6.43	5.76
Al <sub>2</sub> O <sub>3</sub>	14.68	14.40	16.27	14.85	15.27	15.83	14.68	14.38	14.61
MnO	0.00	0.00	0.50	0.06	0.19	0.00	0.00	0.00	0.00
FeO <sub>T</sub>	9.93	5.78	11.90	13.39	10.78	10.94	10.41	11.75	11.96
MgO	20.49	22.77	19.41	16.63	19.74	18.82	17.87	16.58	17.59
CaO	0.36	0.00	0.43	0.00	0.20	0.07	0.00	0.00	0.08
Na <sub>2</sub> O	0.23	0.24	0.30	0.20	1.03	0.47	0.51	0.37	0.39
K <sub>2</sub> O	7.02	8.33	3.41	5.82	6.16	5.74	8.70	7.56	7.65
NiO	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.60	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaO	0.04	0.16	0.42	0.61	0.65	0.32	0.80	0.25	0.57
total **	92.71	93.69	90.74	89.73	93.48	91.18	94.42	91.95	94.24
mg	0.79	0.88	0.74	0.69	0.77	0.75	0.75	0.72	0.79

	SC36-2	SC36-4	SC37-2	SC37-4	SC38-7	SC38-10	SC38-12	SC46-8	SC46-10
Type	PC	PR	PC	MC	PC	M	G	MC	PC
SiO <sub>2</sub>	35.56	35.18	36.82	35.12	39.30	36.86	36.14	36.14	36.02
TiO <sub>2</sub>	6.25	5.32	2.95	5.82	3.20	6.21	4.75	2.85	3.07
Al <sub>2</sub> O <sub>3</sub>	14.71	15.63	15.09	14.59	14.18	14.57	15.14	15.08	14.77
MnO	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.13	0.14
FeO <sub>T</sub>	11.29	13.08	7.87	10.66	5.60	11.22	12.70	7.45	7.11
MgO	18.12	18.55	22.81	18.10	21.89	17.55	16.44	22.83	22.93
CaO	0.10	0.11	0.10	0.00	0.00	0.00	0.00	0.25	0.39
Na <sub>2</sub> O	0.65	0.48	0.41	0.40	0.29	0.62	0.78	0.14	0.29
K <sub>2</sub> O	6.20	5.81	5.67	7.62	9.48	8.62	8.28	5.17	6.28
NiO	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.05	0.54	0.00	0.99	0.00	0.00	1.86	0.43
BaO	0.39	0.52	0.09	0.49	0.00	0.50	0.34	0.00	0.13
total	93.67	94.33	92.32	92.31	94.95	95.65	94.23	91.89	91.44
mg	0.74	0.72	0.84	0.75	0.87	0.74	0.70	0.85	0.85

\* P = phenocryst, M = microphenocryst, G = groundmass, C = core, R = rim

\*\* P<sub>2</sub>O<sub>5</sub> and Rb<sub>2</sub>O, each, are below the limits of detection

Table 1b. Chemical characteristics of the two groups of micas in the Shaw's Cove minette

	range	$\bar{x}$
Group I: high- <i>mg</i> —low-TiO <sub>2</sub> group (N=11)		
wt. % TiO <sub>2</sub>	2.56 – 3.20	2.93
<i>mg</i>	0.81 – 0.88	0.85
wt. % BaO	0.00 – 0.28	0.09
wt. % Cr <sub>2</sub> O <sub>3</sub>	0.28 – 1.86	0.88
wt. % NiO	0.00 – 0.19	0.08
Group II: low- <i>mg</i> —high-TiO <sub>2</sub> group (N=40)		
wt. % TiO <sub>2</sub>	4.03 – 7.96	5.40
<i>mg</i>	0.68 – 0.79	0.73
wt. % BaO	0.00 – 0.80	0.38
wt. % Cr <sub>2</sub> O <sub>3</sub>	0.00 – 0.05	0.00
wt. % NiO	0.00 – 0.05	0.00

where; *e.g.*, Velde, 1969, p. 207; Roden and Smith, 1979, p. 372). There are, however, anomalies that seem to be related to the position of the sample within the sill. Three analyses of micas identified as groundmass crystals from samples near the upper margin of the sill fall within Group 1, although other groundmass micas from the same samples are not anomalous, while three analyses of phenocryst cores from the central coarser-grained portion of the sill have the low *mg* and high TiO<sub>2</sub> content of Group 2 micas. The chemical group into which microphenocrysts fall varies with their location: those from near the margins are in Group 1, those from well within the sill are in Group 2. Whole-rock analyses of samples from a section through the Shaw's Cove sill (Simpson, 1980) do not show any significant differences in bulk TiO<sub>2</sub> content or *mg* value between the minette's central and marginal portions that could account for these anomalies. This lack, however, does not preclude the possibility of small-scale gradients in Mg, Fe, and Ti existing within the liquid at the time of mica crystallization. The anomalies may also be attributable to simple mislabelling. Slower cooling in the center of the sill has allowed groundmass micas to grow nearly to phenocryst size. Phenocryst phlogopites, especially those with poorly developed or unusually narrow rims, from the sill's margins may have been misidentified as groundmass crystals because thin sectioning made them appear smaller than they are and the presence of the rim was not noticed using the microprobe's optical system.

### K<sub>2</sub>O and SiO<sub>2</sub>

K<sub>2</sub>O and SiO<sub>2</sub> contents of most of the micas, both phenocrysts and groundmass, are lower than normal for phlogopites and are positively correlated. The mean K<sub>2</sub>O content of groundmass micas is lower than the mean for phenocrysts, although individual groundmass crystals cover virtually the entire range of K<sub>2</sub>O values, from the lowest to the second highest. For a given silica content, the phenocrysts tend to have less K<sub>2</sub>O than do ground-

mass micas; such a relationship is displayed by, *e.g.*, Velde's (1969) analyses of phenocrysts and groundmass micas in a French minette (Table II, anal. 12 & 13), but the reverse can also apply in other minettes (*cf.* anal. 18 & 19 of her Table II).

Overall mean values for K<sub>2</sub>O (5.59 wt.%) and SiO<sub>2</sub> (34.18 wt.%) are not balanced by correspondingly higher Na<sub>2</sub>O (0.36 wt.%) and Al<sub>2</sub>O<sub>3</sub> (15.23 wt.%) and are significantly lower than previously published values for micas in lamprophyres. For analyses of minette micas in the literature of the last two decades for which both potash

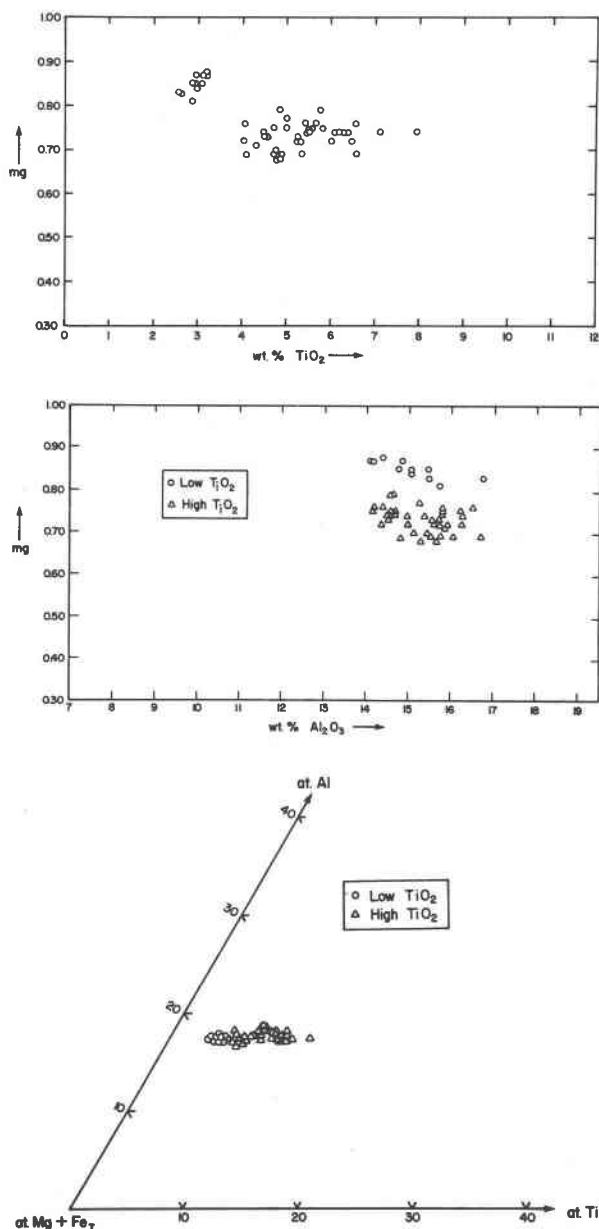


Fig. 1. Chemistry of phlogopites in the Shaw's Cove minette. (a) Covariation of *mg* and wt. % TiO<sub>2</sub>. (b) Covariation of *mg* and wt. % Al<sub>2</sub>O<sub>3</sub>. (c) Atomic proportions of Ti, Al, and (Mg+Fe<sup>2+</sup>).

and silica values are given, means are 9.2 wt.% and 38.6 wt.% respectively ( $N = 58$ ); for micas in lamprophyres other than minettes (50 analyses, a little less than half of which are of micas from kersantites)  $K_2O = 8.4$  wt.%,  $SiO_2 = 36.8$  wt.%. Of the Shaw's Cove micas, 71% have  $K_2O < 7.0$  wt.% and 73% have  $SiO_2 < 36.0$  wt.%, while of the 112 literature values for micas in other lamprophyres including minettes, only 8 have less than 7.0 wt.% potash and 21 have less than 36.0 wt.% silica. Thirty of our 51 analyses are of groundmass micas. In distinction, only 10% of the published mica analyses for lamprophyres are microprobe analyses of groundmass crystals. Because of the differing proportions of groundmass mica analyses in our data set and in the lamprophyre literature, it may not be appropriate to compare mean values. It should be noted, though, that 7 of the 8 literature analyses of lamprophyric micas that show  $K_2O < 7.0$  wt.% do not represent microprobe analyses of groundmass micas but are wet analyses of bulk mica samples; low potash values in these samples certainly cannot be attributed to loss of potassium from the sample under the electron beam of the microprobe. Volatilization of potassium during analysis of our micas is unlikely since only some micas have low  $K_2O$  and identical microprobe conditions prevailed during all mica analyses. Also, under similar conditions there was no loss of sodium, an even more volatile element, from other minerals.

Micas with  $K_2O < 7.0$  wt.% and/or  $SiO_2 < 36.0$  wt.% have been observed in igneous rocks other than lamprophyres, including granitic rocks (*e.g.*, Barrière and Cotten, 1979), leucite-bearing lavas (*e.g.*, Cundari, 1973; Birch, 1978; Thompson, 1978), high-pressure cognate megacrysts (Ellis, 1976), monticellite peridotite and turjaite (Wendlandt, 1977), carbonatites (Gaspar and Wyllie, 1982), ultramafic complexes (Skinner, 1969; Grapes, 1975; Donaldson, 1975), and as phenocrysts and groundmass phases in kimberlites (*e.g.*, Dawson *et al.*, 1970; Giardini *et al.*, 1974; Mitchell, 1978; Smith *et al.*, 1978; Clement *et al.*, 1979; Boctor and Boyd, 1982), as well as in xenoliths in alkaline basalts (Ryabchikov *et al.*, 1982). Some of these micas are especially rich in  $TiO_2$  or BaO. But the existence in minettes of equally titanium- or barium-rich phlogopites with normal amounts of  $K_2O$  and  $SiO_2$  (*e.g.*, Nicholls, 1969) indicates that the enrichment in titanium and barium is not necessarily complemented by an impoverishment in potassium and silicon.

It could be hypothesized that there is either a physical mixture with, interlayering, or an alteration of our mica to an essentially  $K_2O$ -free, more hydrous phyllosilicate. The requirement that the second phase, relative to phlogopite, be poorer in  $SiO_2$ , rich in  $Al_2O_3$ , and not drastically different in  $MgO$ ,  $FeO_T$ ,  $CaO$ , and  $Na_2O$  contents and *mg* ratio eliminates serpentine, talc, and smectites (including saponitic ones) from consideration. Minerals of appropriate composition include chlorites ( $\sim$ clinochlore), septechnorites ( $\sim$ amesite), and vermiculite; all have been reported as weathering or alteration products of phlogopitic micas elsewhere (Deer *et al.*, 1962, p. 48 & 156; Velde,

1969; McCallum *et al.*, 1975; Mitchell, 1978): for example, Skinner (1969) records that  $K_2O$ -poor micas in an ultramafic rock contain up to 15% vermiculite.

Several arguments, however, nullify the proposition that a mixture of phlogopite and some other phyllosilicate exists on anything but a negligible level in the Shaw's Cove micas. First, the micas of this minette microscopically appear fresh and unaltered. Indeed, this is a general characteristic of most micas in lamprophyres (*e.g.*, Velde, 1969). Second, if one uses the analysis of one of our phlogopites whose potash and silica contents correspond to the mean values for these oxides in minettes in general as one end-member and the analysis of a Ti-bearing clinochlore (Deer *et al.*, 1962, Table 25, anal. 28) as the other, approximately 40 wt.% chlorite would have to be mixed with the phlogopite in order to produce the *mean*, not the lowest, potash and silica values of the Shaw's Cove phlogopites! It is inconceivable that such a quantity of chlorite or any similar phase could not be detected optically. Third, X-ray diffraction patterns of Shaw's Cove micas show none of the peaks of either 7-Å or 14-Å chlorites, montmorillonites, talc, or vermiculite; the micas do not respond to either hydration or glycolation. We conclude, therefore, that the low potash and silica contents of many of our micas are real and are not an artifact of analytical technique, alteration, or admixture.

Structural formulae of our micas indicate that nearly two-thirds of the analyses—including phenocrysts and groundmass crystals—have Y parameters in excess of 6.000, the maximum number of octahedral sites (our highest Y value is 6.949, the mean is 6.220), and there is a strong negative correlation between Y and X site occupancies, the latter of which is always less than 2.000 (0.473 to 1.827;  $\bar{x} = 1.261$ ). This suggests that some normally octahedrally-coordinated cations are in the interlayer position. The positive correlation between excess Y ions and the number of tetrahedrally-coordinated aluminum ions provides further support for this and an explanation for the positive correlation between wt.%  $K_2O$  and  $SiO_2$ : low amounts of silicon require high amounts of tetrahedrally coordinated aluminum to complete the sheet structure, but this leads to a charge imbalance that may be offset by substitution of divalent cations (*e.g.*,  $Mg^{+2}$ ,  $Fe^{+2}$ ) for  $K^{+1}$  in the X site. Interestingly, Group 1 micas (high *mg*,  $MgO$ , and  $FeO_T$ ) show a greater number of tetrahedrally-coordinated aluminum ions than do Group 2 micas. Of the potash- and silica-poor mica analyses in the literature, only one a "platy phlogopite replacing hornblende" (Deer *et al.*, 1962, anal. 6), combines the excess of Y cations with the X-site deficiency that characterizes the majority of the Shaw's Cove micas.

However, as even those micas that do not have an excess of Y cations still have less than 2.000 X cations, many of the mica analyses in Table 1a have low totals, and there is a rough positive correlation between wt.%  $K_2O$  and volatile-free totals, it is possible that there is

Table 2. Mean composition of micas in minettes, excluding Shaw's Cove micas (N=62)

	wt. %	range
SiO <sub>2</sub>	38.6	38.4 - 41.7
TiO <sub>2</sub>	4.5	1.4 - 11.3
Al <sub>2</sub> O <sub>3</sub>	13.4	9.7 - 18.0
FeO <sub>T</sub>	7.9*	4.8 - 13.1*
MgO	20.5*	14.7 - 25.4*
K <sub>2</sub> O	9.2	4.4 - 10.6
Na <sub>2</sub> O	0.5	0.0 - 1.1
mg	0.82*	0.67 - 0.90*

\*excluding 6 anomalous micas from the Pendennis minette (see text)

some water or hydronium ion substitution in the interlayer position.

We believe that these variations in the potash and silica contents of the Shaw's Cove micas are predominantly primary and reflect the relative activities of these and other components that may enter the phlogopite at the time of its crystallization. That the activities can vary widely in minette liquids is illustrated especially well by the groundmass phlogopites for which the availability of components is complicated by the simultaneous crystallization of other groundmass phases.

### Comparison with micas from other minettes

Ranges and mean values of the important oxides in analyses of 62 micas of minettes in the literature are presented in Table 2 (see Appendix for sources of data) and the covariation of the major atoms that may occur in octahedrally coordinated sites—Mg, Fe, Ti, and Al—is shown in Figure 2a,b,c. Like the Shaw's Cove micas, micas in other minettes are phlogopites of moderate aluminum and high titanium contents but are richer in silica and potash; the lack of a correlation between *mg* and Al<sub>2</sub>O<sub>3</sub> (Fig. 2b) presumably reflects an absence of Al ions in octahedrally-coordinated sites. One of these micas (phenocryst core, mafic minette ring dike, Buell Park, Navajo Indian Reservation, Arizona; Roden and Smith, 1979, Table 3, rock BPR-5) is among the most Ti-rich micas (TiO<sub>2</sub> = 11.3 wt.%) known to us regardless of rock type! This specimen also has the lowest SiO<sub>2</sub> concentration (33.9 wt.%) of any minette mica but has a normal alumina content.

Analyses of five minette micas are chemically identical in all respects to those of Shaw's Cove micas; these micas occur in minettes from southernmost East Germany (Kramer, 1976, Table 8, anal. 152, bulk sample), eastern France (Velde, 1969, Table II, anal. 5, bulk analysis of phenocrysts), southwestern Scotland (Gallagher, 1963, Table II, anal. 2, bulk sample), and the Navajo Indian Reservation of southwestern U.S.A. (Velde, 1969, Table

III, anal. 6-A-5, bulk sample; Nicholls, 1969, Table 6, anal. 666-P, microprobe analysis of a phenocryst). Interestingly, the analyses of the German and Scottish specimens, like many of those from Shaw's Cove, have low K<sub>2</sub>O and SiO<sub>2</sub> values.

Although color zoning and the associated chemical bimodalism is observed in virtually all those micas analyzed by microprobe, the boundaries of the two chemical groups vary from geographical area to area and even from minette to minette within a swarm. Considering the

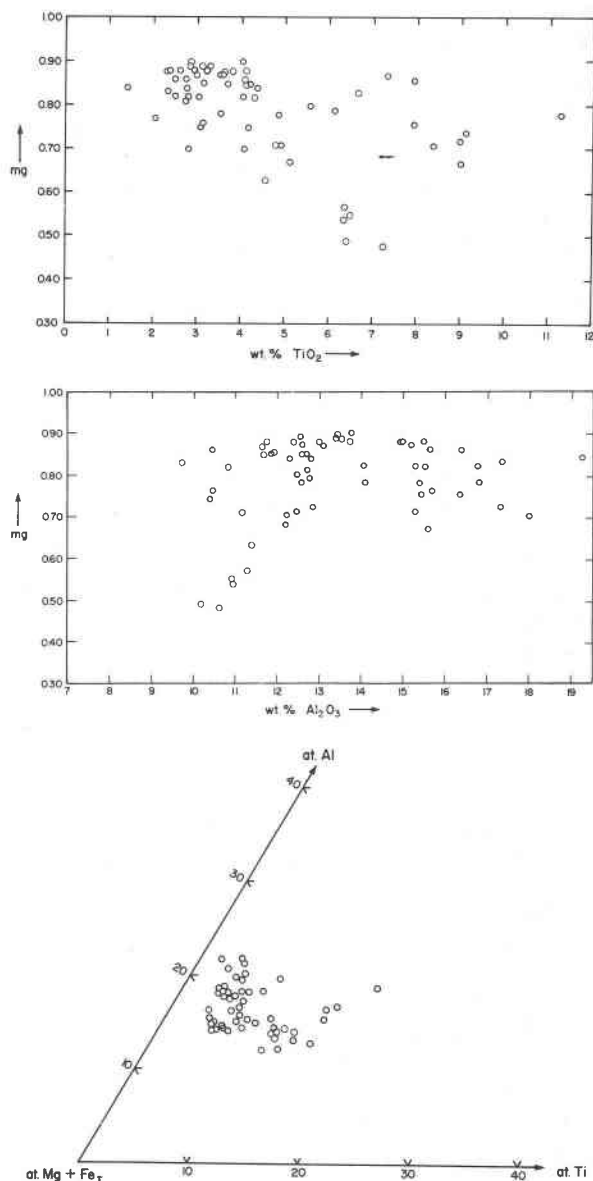


Fig. 2. Chemistry of phlogopites in minettes other than the Shaw's Cove minette; see Appendix for sources of data. (a) Covariation of *mg* with wt.% TiO<sub>2</sub>. (b) Covariation of *mg* with wt.% Al<sub>2</sub>O<sub>3</sub>. (c) Atomic proportions of Ti, Al, and (Mg+Fe<sup>2+</sup>). Values for *mg* calculated using all iron as FeO.

entirety of the minette mica analyses, it is not possible to predict whether a given mica sample will have a relatively high or low  $\text{TiO}_2$  content merely by knowing whether it is a phenocryst core or a groundmass crystal (or phenocryst rim); the same applies to prediction of the  $mg$  value. For example, in one minette from the Navajo area a groundmass mica contains 4.84 wt.%  $\text{TiO}_2$  while a mica phenocryst from another minette in the same volcanic field has 7.69% (Nicholls, 1969, Table 6, anal. 672-GM and 649F-P). Nonetheless, for microprobe analyses of single crystals or portions thereof, the following generalizations may be stated: from core to rim to groundmass,  $mg$  decreases while  $\text{TiO}_2$  increases (except in rare cases of reverse zoning of core and rim) and groundmass micas nearly always have  $mg < 0.80$  and  $\text{TiO}_2 > 4.00$  wt.%.

Sodium, a minor but ever-present constituent of minette micas, is slightly less abundant in the Shaw's Cove micas than in those of other minettes ( $\bar{x} = 0.36$  and  $0.5$  wt.% respectively) though the range of values is nearly identical. The overall mean  $\text{Na}_2\text{O}$  content in all minette micas is  $0.43$  wt.%.

Only rarely have minette micas been analyzed for trace elements. NiO and, in particular,  $\text{Cr}_2\text{O}_3$  may reach sizeable concentrations in phenocryst cores while in phenocryst rims and groundmass crystals BaO commonly exceeds  $0.1$  wt.% and may be more than an order of magnitude greater. Overall means, including Shaw's Cove analyses, are NiO =  $0.02$  wt.% ( $N = 76$ ),  $\text{Cr}_2\text{O}_3 = 0.30$  wt.% ( $N = 82$ ), BaO =  $0.48$  wt.% ( $N = 86$ ). We have not analyzed our phlogopites for fluorine, though minette micas are known to contain significant amounts; literature values (Némec, 1968; Nicholls, 1969; Kramer, 1976; Luhr and Carmichael, 1981) have a mean of  $1.11$  wt.% F ( $N = 24$ ) and fluorine contents may increase or decrease from phenocryst core to rim to groundmass (see also Jones and Smith, 1982). Luhr and Carmichael (1981) report fluorine contents of  $\leq 1.52$  wt.% in phlogopite phenocryst rims,  $F/(F + \text{OH}) = 0.1\text{--}0.2$  for phenocrystic phlogopites in general, and  $4.85$  wt.% F in a groundmass phlogopite in the minettes of Colima, Mexico. Because of the marked variations of all these trace elements (or oxides) between phenocryst cores and rims and groundmass crystals, mean values are of negligible use.

The unusual peralkaline but silica-oversaturated Pendennis minette at Falmouth, Cornwall, England (Hall, 1982) contains titaniferous phlogopites whose iron-rich rims (Table III, anal. 7–12) are unlike micas in all other minettes and all other mafic rocks considered here (see below). We have designated them as "anomalous" because they have lower  $mg$  values than "normal" minette micas and  $\text{Al}_2\text{O}_3$  contents matching those of the most Al-poor minette micas, but have  $\text{TiO}_2$  contents that are high but in the minette-mica range (see Fig. 2a,b). For five of these six analyses,  $mg = 0.48\text{--}0.57$ ,  $\text{Al}_2\text{O}_3 = 10.20\text{--}11.97$  wt.%, and  $\text{TiO}_2 = 6.36\text{--}7.23$  wt.%; the sixth (anal. #7;  $mg = 0.63$ ,  $\text{Al}_2\text{O}_3 = 11.39$ ,  $\text{TiO}_2 = 4.57$ ) is transitional to normal minette micas.

Although Hall (1982), Barton (1979), and Arima and Edgar (1981) suggest that the composition, especially the alumina content, of micas in mafic potassic rocks is a reflection of the composition of the magma from which they crystallized, the nature of this relationship is not clear for minettes. For the Pendennis minette, molecular proportions  $[(K + \text{Na})/\text{Al}] = 1.11$ ,  $mg = 0.64$ , and  $\text{Al}_2\text{O}_3 = 10.4$  wt.% (after correcting for  $\text{CO}_2$ ); yet a metaluminous and silica-undersaturated minette in the Navajo volcanic field with  $mg$  value similar to that of the Pendennis minette (mol. prop.  $[(K + \text{Na})/\text{Al}] = 0.78$ ,  $mg = 0.67$ ,  $\text{Al}_2\text{O}_3 = 10.7$  wt.%; Nicholls, 1969, Table 10, rock 649F) carries groundmass phlogopite with  $mg = 0.76$  and  $\text{Al}_2\text{O}_3 = 10.5$  wt.% (*op. cit.*, Table 6)—much higher  $mg$  but the same  $\text{Al}_2\text{O}_3$  as in the anomalous rims of the Pendennis micas—while the peralkaline but more magnesian Sisco minette of Corsica (mol. prop.  $[(K + \text{Na})/\text{Al}] = 1.04$ ,  $mg = 0.73$ ,  $\text{Al}_2\text{O}_3 = 12.1$  wt.%; Velde, 1965) is host to relatively aluminum-rich phlogopites with high  $mg$  values ( $\text{Al}_2\text{O}_3 = 13.8$  and  $15.0$  wt.%,  $mg = 0.90$  and  $0.88$ ; Velde, 1969, Table II, anal. 2 & 3). The Holsteinsborg minettes are silica-saturated to -oversaturated but more magnesian and even more Al-poor than the Pendennis minette and are remarkably peralkaline (average mol. prop.  $[(K + \text{Na})/\text{Al}] = 1.39$ ,  $mg = 0.74$ ,  $\text{Al}_2\text{O}_3 = 7.8$  wt.% after correcting for  $\text{CO}_2$ ; Scott, 1979, Table 4); their phlogopites have high  $mg$  values ( $0.87$  and  $0.83$ ) and one of them (*op. cit.*, Table 3, anal. 137) has the lowest  $\text{Al}_2\text{O}_3$  ( $9.70$  wt.%) of any minette mica. On the other hand, one of the Colima minettes, which have  $mg$  values similar to those of the Holsteinsborg dikes but more  $\text{Al}_2\text{O}_3$  and are metaluminous rather than peralkaline (mol. prop.  $[(K + \text{Na})/\text{Al}] = 0.69\text{--}0.80$ ,  $mg = 0.70\text{--}0.75$ ,  $\text{Al}_2\text{O}_3 = 11.1\text{--}12.5$  wt.%; Luhr and Carmichael, 1981, Table 3), contains groundmass phlogopite ( $\text{Al}_2\text{O}_3 = 10.8$  wt.%,  $mg = 0.82$ ; *op. cit.*, Table 9, anal. 100B) that has a much higher  $mg$  value but  $\text{Al}_2\text{O}_3$  as low as that of the anomalous micas in the peralkaline Pendennis minette. Furthermore, as the minette magma evolves and the mica's  $mg$  value decreases from phenocryst core to rim and/or groundmass, the  $\text{Al}_2\text{O}_3$  content of the mica may decrease (*e.g.*, Hall, 1982; Roden and Smith, 1979, Table 3, micas in rocks BPR-5 and BP-51; Luhr and Carmichael, 1981, Table 9, micas in rock 104; Nicholls, 1969, Table 6, micas in rocks 672 and 681), stay the same (Nicholls, 1969, Table 6, micas in rock 649F), increase (this work, Table 1, anal. 30-11, 17 and 36-2, 4; Roden and Smith, 1979, Table 3, micas in rock BP-35), or even first decrease then increase (Nicholls, 1969, Table 6, micas in rock 649C).

### Comparison with micas in other igneous rocks

Minette micas are unlike those of common granitoids, their extrusive equivalents, pegmatites, or metamorphic rocks (*e.g.*, Velde, 1969; Kramer, 1976) and none of these rocks is likely to be directly connected to minettes genetically. Although the petrogenesis of lamprophyres

*sensu lato* is still controversial, recent studies increasingly indicate that the liquids from which minettes and at least some other lamprophyres have crystallized are from the mantle and may be generated by processes, under conditions, and/or from source rocks related (to varying degrees) to those responsible for (ultra)potassic rocks and kimberlites (*e.g.*, Bachinski and Scott, 1979, 1980; Ehrenberg, 1979, 1982; Roden and Smith, 1979; Luhr and Carmichael, 1981; Mitchell, 1981; Paul and Potts, 1981; Roden, 1981; Hall, 1982; Platt and Mitchell, 1982; Rogers *et al.*, 1982). It is therefore of interest to compare the phlogopites of minettes with the micas of these rocks and xenoliths from the mantle and lower crust.

For this comparison 353 mica analyses from rocks other than minettes were collected from the literature of 1966–1982 and a few older papers. Subdivided by rock type into five groups, these analyses include the following: 50 from lamprophyres other than minettes; 68 from a variety of ultramafic to intermediate, intrusive and extrusive, potassic and ultrapotassic rocks (madupites, orendites, wyomingites, fitzroyites, cedricites, woldingites, jumillites, verites, fortunites, leucitites, shoshonites, shonkinites, biotitites, *etc.*);<sup>2</sup> 113 from kimberlites; and 122 from high-pressure xenoliths (51 of these are in minettes, nephelinites, basanites, and other alkaline volcanic rocks, while 71 are in kimberlites and diamonds). Combined with the 113 minette phlogopites, including those of Shaw's Cove, 466 mica analyses are considered here.

The analyses are presented in a series of *mg* vs. wt.% TiO<sub>2</sub> diagrams (Figs. 3 to 7) like those used above for the minette micas. On each of the diagrams the superimposed long curved lines indicate the field in which plot micas from all minettes (N = 107) including the Shaw's Cove but excluding the anomalous Pendennis micas of Figures 1a and 2a: the broken line encloses the field containing 93%, the solid line encloses 100% of these; the field of the five anomalous and one transitional Pendennis micas is indicated separately. To be conservative, the following comparisons are presented with reference to the broken lines (main minette mica field) unless explicitly stated otherwise. Diagrams of *mg* vs. wt.% Al<sub>2</sub>O<sub>3</sub> and atomic proportions of (Mg + Fe<sup>2+</sup>)-Ti-Al were also constructed for all the sets of analyses. Although these latter two sets of figures are not presented here for the sake of economy, when we say below that certain micas fall "within the minette field" or make equivalent statements we are referring to the minette field on all three diagrams. In terms of the four components encompassed by these sets of diagrams as well as wt.% SiO<sub>2</sub>, K<sub>2</sub>O, Na<sub>2</sub>O, and trace element concentrations, it is important to note that *none* of the five groups of micas is wholly distinct from minette micas. (Considering the errors associated with analyzing for Na<sub>2</sub>O by electron microprobe, especially when it is

present in such minimal amounts as in phlogopites, differences in Na<sub>2</sub>O contents may not be significant). It must be stressed, though, that each of the five groups of rocks also contains micas that differ from those of minettes and/or have differing trends of compositional evolution (see also Mitchell, 1981, and Arima and Edgar, 1982).

### Lamprophyres other than minettes (Fig. 3)

The micas of other lamprophyres tend to have lower *mg* values, the same or slightly lower TiO<sub>2</sub>, the same Na<sub>2</sub>O (although micas of kersantites as a distinct subgroup have slightly higher), and somewhat higher Al<sub>2</sub>O<sub>3</sub>. Of those analyses (26) that plot within the minette field on all three diagrams, about half are of micas from kersantites (Métais, *et al.*, 1962, Table 2, anal. 1; Velde, 1969, Table 4, anal. 4, 7, 8, 9, 12, 15; Strong and Harris, 1974, Table 2, anal. 3; Kramer, 1976, Table 8, anal. 205, 217, 271). The others are from monchiquites and camptonites (Nicholls, 1969, Table 6, anal. 618-P; McHone, 1978, Table III-4, anal. BU-1, BU-2; Rock, 1978, Table 9, anal. 2; Cooper, 1979, Table 1, anal. LG-core and O-core), damkjernite (monchiquite?); (Griffin and Taylor, 1975, Table 3, anal. 7), three un-named lamprophyres (Rimsaite, 1971, Table 1, anal. 8-PH, 9-PH; Janse, 1977, Table 1, anal. 4), and Precambrian alnöitic ultrabasic lamprophyres (Platt and Mitchell, 1982, Table 3, anal. 1, 2, 3, 6). Approximately half of these minette-like micas have the low SiO<sub>2</sub> and K<sub>2</sub>O contents commonly seen in minette micas. Three minette-like micas, however, do not truly match minette micas if Na<sub>2</sub>O and trace element contents are taken into consideration: the two camptonite specimens from New Zealand (Cooper, 1979) contain significantly more Na<sub>2</sub>O than any minette mica while the mica of the biotite monchiquite from Arizona (Nicholls, 1969) has a BaO content (6.20 wt.%) over twice as great as the

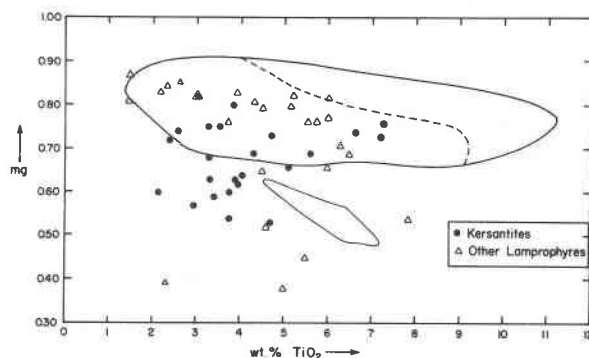


Fig. 3. Covariation of *mg* and wt.% TiO<sub>2</sub> in micas of lamprophyres other than minettes (total iron calculated as FeO); see Appendix for sources of data. Excluding the 6 anomalous Pendennis micas, the larger broken line indicates the field defined by 93% of the minette micas of Fig. 1a and 2a, the larger solid line encloses 100% of these; the anomalous Pendennis micas' field is the small area defined by the solid line below the main minette-mica field; see text.

<sup>2</sup> For convenience this group will be referred to hereinafter as "potassic rocks".



maximum reported for a mica from a minette. (The highest value known to us is 10.3 wt.% BaO in the core of a phlogopite from the Jacupiranga carbonatite's sövite facies; Gaspar and Wyllie, 1982).

#### Potassic rocks (Fig. 4)

Because of the diversity of this group of rocks, general comparisons between their micas and those of minettes are not possible; instead reference must be made to subgroups. Two of these, *biotitites* (2 analyses; Boettcher, 1967, Table 3) and *shonkinites* (5 analyses; Nash and Wilkinson, 1970, Table 5; Langworthy and Black, 1978, Table 1) carry micas that are not at all like those of minettes. The micas of the other subgroups are minette-like to varying degrees. Of the 13 mica analyses that fall within the minette field, one shows higher BaO than the phlogopites of minettes and another higher Na<sub>2</sub>O.

**Ultrapotassic rocks (lamproites)** (40 analyses). The micas of ultrapotassic volcanic rocks or lamproites are of particular interest because these rocks are geochemically much like minettes (e.g., Carmichael *et al.*, 1974; Mitchell, 1981). The micas of two of the ultrapotassic lavas of southeastern Spain (verite and fortunite; Velde, 1969, Table 3, anal. 12-A-5 and 14-A-7) are identical to minette micas, but the jumillite micas (Borley, 1967, Table II; Carmichael, 1967, Table 6), although as rich in TiO<sub>2</sub> as the most titaniferous minette micas, are Al-deficient. In contrast, the micas from the famous Leucite Hills, Wyoming (U.S.A.) locality (Cross, 1897; Carmichael, 1967, Table 6; see also Barton, 1979) are wholly distinct from minette micas though similar in Na<sub>2</sub>O and trace element contents: orendite and wyomingite micas have higher *mg* values and lower TiO<sub>2</sub> while the madupite mica has lower Al<sub>2</sub>O<sub>3</sub>. In the equally famous West Kimberley province of Australia (Carmichael, 1967, Table 6; Mitchell, 1981) the micas are very TiO<sub>2</sub>-rich, have higher *mg* values than most minette micas of equivalent TiO<sub>2</sub> content, and plot

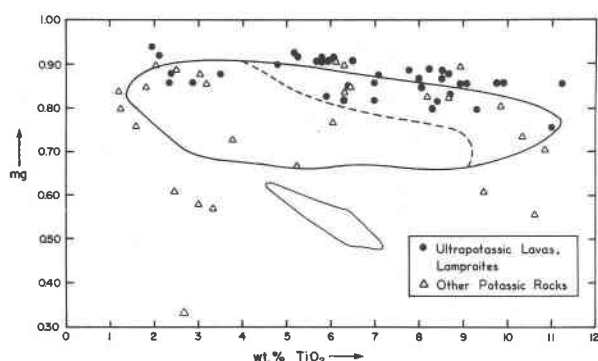


Fig. 4. Covariation of *mg* and wt.% TiO<sub>2</sub> in micas of ultramafic to intermediate potassic and ultrapotassic igneous rocks other than kimberlites and lamprophyres and xenoliths therein; see Appendix for sources of data. Curved lines indicate extent of minette-mica field as explained in caption to Fig. 3 and text.

within or above the borders of the minette field of Figure 4; they all, however, have Al<sub>2</sub>O<sub>3</sub> contents lower than or equal to the most Al-poor minette micas, and trace elements in the same concentrations as in minette micas. (Nearly three-quarters of the analyses of micas from ultrapotassic rocks plotted on Fig. 4 are from West Kimberley).

The chemistry of the lamproites at Smoky Butte, Montana (U.S.A.) is similar to that of the Australian West Kimberley rocks (Velde, 1975). A bulk analysis of Smoky Butte phlogopites from a "Type III" lamproite (*op. cit.*, Table 3) is identical to analyses of high-TiO<sub>2</sub> minette micas. The other two analyses are of a core and rim of extremely Ti-rich (TiO<sub>2</sub> = 11.3 and 11.1 wt.%) phlogopite; the rim is poorer in Al<sub>2</sub>O<sub>3</sub> (8.9 wt.%) and the core has a higher *mg* value (0.86) than equally titaniferous minette micas. None of these micas was analyzed for trace elements. A lamproite (called a "potash trachyte" by Nicholls, 1969, rock 643) in the Navajo area of Arizona is probably an extrusive felsic minette, so it was predictable that its phlogopite phenocryst would be identical to minette micas in all respects.

**Shoshonites** (2 analyses). Micas from two shoshonitic volcanic rocks (latites) are minette-like though one of them has higher Na<sub>2</sub>O than minette micas; trace element data are not given (Joplin *et al.*, 1972, Table V).

**Leucite-bearing lavas** (7 analyses). All but one of these micas are rich in TiO<sub>2</sub>. Five of the 7 differ considerably from the micas of minettes (Cundari, 1973, Table V, anal. BQ-PEGM and BEH-B; Birch, 1978, Table 5; Thompson, 1978, Table 2, anal. 5), but the other two (Cundari, 1973, anal. BEH-A and CND-6) are identical to high-TiO<sub>2</sub> minette micas and both have Na<sub>2</sub>O and trace element concentrations within the minette-mica range.

**Other potassic rocks** (12 analyses). Three of the six analyzed phlogopites from Precambrian hypabyssal potassic ultramafic rocks (phlogopite pyroxenites and phlogopite peridotites) in the Gardar province of south Greenland (Upton and Thomas, 1973, Table 3, anal. 1, 2, 6) match high-TiO<sub>2</sub> minette micas in their major and minor oxides and Cr<sub>2</sub>O<sub>3</sub> and BaO contents (there are no analyses for Na<sub>2</sub>O). The remaining three phlogopites are minette-like in all respects save that they are impoverished in FeO<sub>T</sub> and consequently have marginally higher *mg* values (0.90 and 0.91) than minette micas of equivalent TiO<sub>2</sub> content. Upton and Thomas believe that these rocks—which in their trace element chemistry are reminiscent of ultrapotassic rocks, minettes, and kimberlites—crystallized from magmas formed by the fractionation of olivine from kimberlitic liquids.

One of the three analyses of barian phlogopites in *monticellite peridotites* and *turjaite*s at Haystack Butte, in the potassic Highwood Mountains province of Montana (Wendlandt, 1977, Table 25) plots within the minette field but contains far too much BaO (3.91 wt.%) to be minette-like; the other two micas are unlike minette micas.

Lastly, three representative analyses of phlogopite megacrysts (phenocrysts) from an *alnöitic breccia* in the Solomon Islands (Dawson *et al.*, 1978, Table 2, anal. 1, 2, 3) are chemically indistinguishable from phlogopites in minettes on the basis of all oxides for which data are presented, though their analysis #1 plots right on the border of the minette field of Figure 4.

### Kimberlites (Fig. 5)

Generally, kimberlite phlogopites have higher *mg* values and  $\text{SiO}_2$ , lower  $\text{TiO}_2$ , and similar or lower  $\text{Al}_2\text{O}_3$  contents than minette micas and many plot outside the minette field, some even off the range of the diagrams. Strictly minette-like micas, however, occur in kimberlites from Somerset Island, Northwest Territories, Canada (Clarke and Mitchell, 1975, Table 1, anal. 5; Mitchell, 1978, Table 3, anal. 2; Mitchell, 1979, Table 3, anal. 2, 3, 4, 5); Ontario, Canada (Rimsaite, 1971, Table 1, anal. 11-PH, and Table 2, anal. II, III; Smith, *et al.*, 1978, Table 3, anal. 5, and Table 4, anal. 8a to 8f); Arkansas, U.S.A. (Giardini *et al.*, 1974, Table 1, brown mica from light green kimberlite); western Greenland (Emeleus and Andrews, 1975, Table 2, anal. 39651/M12; Scott, 1979, Table 3, anal. 129); and various localities in South Africa (Smith, *et al.*, 1978, Table 3, anal. 6b, 7c, and Table 4, anal. 5b, 6b, 7c, 10f, and Table 5, anal. 1b, 4a; Boettcher *et al.*, 1977, and 1979, Table 1, anal. KB-5-1-A-rim, Kb-5-1-B-rim, Kb-5-1-C, Kb-5-13-rim; Clement *et al.*, 1979, Table 3, anal. 7; Boctor and Boyd, 1982, Table 2, anal. 4). Nearly all the kimberlites containing minette-like mica are micaceous kimberlites or, in the terminology recommended by Skinner and Clement (1979), phlogopite kimberlites.

Groundmass crystals (including both "Type I" and "Type II" of Smith *et al.*, 1978) and secondary rims of large phlogopites account for approximately three-quarters of the minette-like micas in kimberlites, but unzoned pre-fluidization phenocrysts (or megacrysts) of the Canadian Arctic's kimberlites (Clarke and Mitchell, 1975, *loc.*

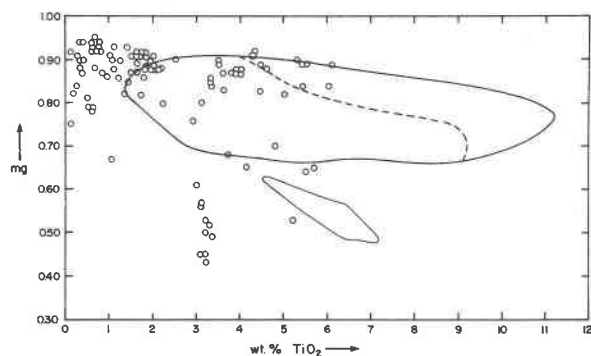


Fig. 5. Covariation of *mg* and wt.%  $\text{TiO}_2$  in micas of kimberlites (excluding xenoliths therein); see Appendix for sources of data. Curved lines indicate extent of minette-mica field as defined in caption to Fig. 3 and text.

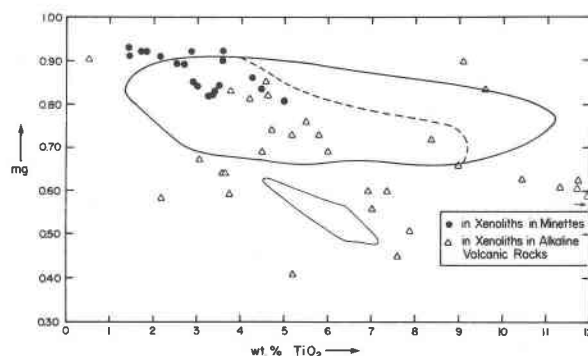


Fig. 6. Covariation of *mg* and wt.%  $\text{TiO}_2$  in micas of high-pressure xenoliths in mafic alkaline volcanic rocks other than kimberlites; see Appendix for sources of data. Curved lines indicate extent of minette-mica field as defined in caption to Fig. 3 and text.

*cit.*; Mitchell, 1978, *loc. cit.*; Mitchell, 1979, *loc. cit.*) and one from the South African DeBeers pipe (Boettcher *et al.*, 1979, Table 1, anal. Kb-5-1-C) also plot within the minette field. It would appear that the micas being sought by Smith *et al.*, (1978, p. 970) and Mitchell (1979, p. 165) that are chemically comparable to their kimberlite micas are to be found in minettes.

### Xenoliths in alkaline rocks (Fig. 6)

Most of the 51 micas in this category have *mg* values lower than or in the same range as minette micas (five have higher); all the other oxides of importance are within the minette range with the exception of  $\text{TiO}_2$  in six megacrysts from Mongolian alkaline basalts (Ryabchikov *et al.*, 1982): these micas have 9.0–12.2 wt.%  $\text{TiO}_2$  and are the most Ti-rich micas known to us from any rock type anywhere. Micas matching those in minettes are found in peridotite and pyroxenite xenoliths in alkaline lavas or pyroclastic rocks from southwest Uganda (Lloyd and Bailey, 1975, Table 2, anal. S23-214, S23-209), Victoria, Australia (Ellis, 1976, Table 3, anal. 7), the West Eifel area of West Germany (Aoki and Kushiro, 1968, Table 4, anal. 2; Becker, 1977, Table 3, anal. GM29, GM17, ME11), Paramore Crater, Arizona, U.S.A. (Evans and Nash, 1979, Table 4, anal. PC76-2), and the Lashaine Volcano, Tanzania (Dawson *et al.*, 1970, Table 7, anal. 2).

Twelve of 19 analyses of phlogopites from garnet lherzolite and megacrystalline nodules in minette plugs or diatremes in the Navajo field of northwestern Arizona and contiguous parts of New Mexico, U.S.A. (Ehrenberg, 1979, Table 3, anal. 144TH, 175TH; Ehrenberg, 1982, Table 8, anal. YA78, 710, 171, 174, X078-1, X078-2, B712, F077, 249, R078) are wholly minette-like. The other seven phlogopites narrowly miss being minette-like by having *mg* values marginally higher than those of minette micas of equivalent  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  contents (two have less titania than any minette mica).

Of all the micas in xenoliths in alkaline rocks, the phlogopites in the xenoliths in minettes, on average, have simultaneously the lowest  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  contents and highest  $mg$  values (in this latter respect they are virtually the "least evolved" micas in this group). When compared to the micas in kimberlites (previous section) the micas in xenoliths in minettes are seen to be identical to many Type II-groundmass micas (Smith *et al.*, 1978, Table 4) and secondary rims on phenocrysts or megacrysts (*e.g.*, Boettcher *et al.*, 1979, Table 1, anal. Kb-5-1-rim and Kb-5-13-rim). They also are comparable to many of the phlogopites occurring in peridotite xenoliths in kimberlites (next section).

### Xenoliths in kimberlites (Fig. 7)

Three of these analyses are of micas included in diamonds (Giardini *et al.*, 1974; Prinz *et al.*, 1975; Gurney *et al.*, 1979) and are dissimilar to analyses of minette micas.

Most of the micas in high-pressure xenoliths in kimberlites are wholly distinct from minette micas: they have lower  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ , higher  $\text{SiO}_2$ , and higher  $mg$  values. These chemical characteristics are typical of "primary" phlogopites (*e.g.*, Carswell, 1975, Table 1) and phlogopites in the MARID suite (Aoki, 1974, Table 1; Dawson and Smith, 1977, Table 2).<sup>3</sup> Some micas in xenoliths in kimberlites, however, are identical to minette micas in all respects. These minette-like phlogopites are predominantly described as being of "secondary" mantle origin ("secondary-textured") and commonly occur as rims on earlier phlogopites or other minerals in eclogites or deformed (sheared) garnet peridotites. One of these micas occurs in a xenolith included in the Peuyuk C kimberlite of Somerset Island, Canada (Clarke and Mitchell, 1975, Table 1, anal. 6), the others are in xenoliths in South African kimberlites (Boettcher *et al.*, 1979, Table 1, anal. Kb-8-8-rim, Kb-9-9-A-rim, Kb-9-9-B-rim, B-16-7; Danchin, 1979, Table 2, anal. RVD-152, RVD-501; Rawlinson and Dawson, 1979, Table 6, anal. BD2027-core; Jones *et al.*, 1982, Table 5, anal. 10c, 11a, 12a, 12b).

An additional two micas, one in an eclogite nodule (Aoki and Kushiro, 1968, Table 4, anal. 4) and one forming a secondary rim on an earlier phlogopite in a peridotite xenolith (Boettcher *et al.*, 1979, Table 1, anal. Kb-5-10-rim), qualify as minette-like on Figure 7 and the  $mg$  vs. wt.%  $\text{Al}_2\text{O}_3$  diagram but fall just outside the lower-left boundary of the minette field of the atomic  $(\text{Mg} + \text{Fe}^{2+})\text{-Ti-Al}$  triangular diagram.

Three minette-like micas are found not in clearly mantle-derived xenoliths but in two lower-crustal garnet granulites and a garnet websterite in kimberlites in north-eastern Lesotho where they appear to be in equilibrium

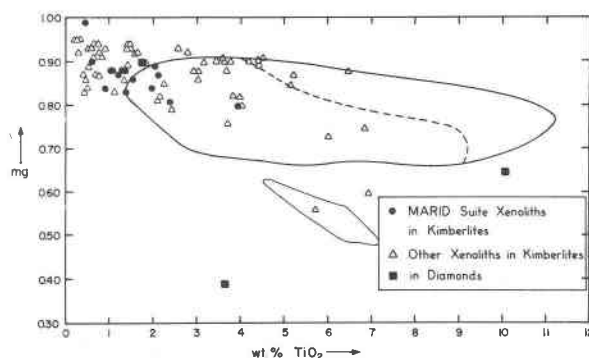


Fig. 7. Covariation of  $mg$  and wt.%  $\text{TiO}_2$  in micas of high-pressure xenoliths in kimberlites; see Appendix for sources of data. Curved lines indicate extent of minette-mica field as defined in caption to Fig. 3 and text.

with the anhydrous phases in the xenoliths (Griffin *et al.*, 1979, Table 4, anal. K3, LQ1, LT2). A mica from a garnet websterite xenolith from the Monastery Mine, South Africa (*loc. cit.*, anal. PHN2630/1) plots in the field of the anomalous micas of the Pendennis minette and matches these micas in all respects save that it has an elevated  $\text{Al}_2\text{O}_3$  content.

### Discussion

As micas whose compositions are essentially identical may have formed under similar physical and/or chemical conditions, it is of petrogenetic significance that minette micas match many micas in the diverse groups of mantle-derived rocks discussed above; the chemical identity is yet another piece of evidence that the liquids from which minettes crystallize are themselves mantle-derived. Those minette mica analyses that are clearly identified as representing the cores of phenocrysts have  $\text{TiO}_2$  concentrations of 2.0–11.3 wt.% and  $mg$  values of 0.74 to 0.90. We assume that these cores crystallized at elevated subcrustal pressures.

High-pressure experiments of, *e.g.*, Edgar *et al.*, (1976, 1980), Ruddock and Hamilton (1978, and pers. comm., 1978) Ryabchikov and Green (1978), and Barton and Hamilton (1982) have demonstrated that phlogopites are liquidus or early-crystallizing phases in a variety of potassic hydrous  $\pm$  carbonate-bearing systems (including a model minette) at pressures of 10–35 kbar, temperatures of 1150–1300°C,  $f_{\text{O}_2}$  between the NNO and HM buffers, and molar  $\text{CO}_2/(\text{CO}_2 + \text{H}_2\text{O})$  ratios of 0.00 to 0.50. Phlogopites produced in these studies have  $mg$  values of 0.82–0.90 and  $\text{TiO}_2$  contents of 1.8 to 8.1 wt.% (the phlogopite with the highest titania content was produced under conditions of  $T = 1300^\circ\text{C}$ ,  $P = 30$  kbar, 2.4 wt.%  $\text{H}_2\text{O}$  and 5.9 wt.%  $\text{CO}_2$ ,  $\text{CO}_2/(\text{CO}_2 + \text{H}_2\text{O}) = 0.50$ ). Some of the primary (as opposed to quench) phlogopites crystallized by Edgar *et al.*, (1976, Tables 3 & 5; 1980, Table 8) and Ryabchikov and Green (1978, Table 3) are chemically

<sup>3</sup> It should be noted, however, that MARID micas cannot be separated from minette micas on the  $\text{NiO}$  vs.  $mg$  or  $\text{Cr}_2\text{O}_3$  vs.  $\text{FeO}_T$  diagrams used by Dawson and Smith (1977, Fig. 6).

identical to cores of minette-mica phenocrysts (as well as other minette micas). In attempting to ascertain the conditions under which minette micas may have crystallized in the light of these experimental studies, the main difficulty lies in separating the effects of temperature, pressure,  $f_{O_2}$ , and fluid and liquid compositions. These studies demonstrate that, under mantle conditions, phlogopite crystallizes early only from  $H_2O$ -rich,  $CO_2$ -poor systems and the  $TiO_2$  content of the phlogopite increases with increasing  $f_{O_2}$  ( $Fe^{+3}$  content of melt), decreasing pressure,<sup>4</sup> decreasing water content of the system, and decreasing  $mg$  value of the crystals and liquid; increasing  $CO_2$  content of the system lowers the temperature at which phlogopites crystallize. The consensus is that temperature and, perhaps more importantly,  $f_{O_2}$  are the major controls on  $TiO_2$  content (see also Arima and Edgar, 1981). It therefore would appear that minette micas, which are notably rich in  $TiO_2$ —as well as some of the micas in certain other lamprophyres, potassic rocks, kimberlites (phenocryst rims and groundmass, largely), and high-pressure xenoliths in alkaline volcanic rocks, and "secondary metasomatic" micas—crystallized under higher  $f_{O_2}$  conditions and/or higher temperatures than most "primary," "primary metasomatic," and MARID-suite micas in kimberlites and xenoliths in kimberlites.

Luhr and Carmichael (1981) report equilibration temperatures (based on the partitioning of oxygen isotopes between olivine, pyroxene, and magma) of 1070° to 1200°C and  $f_{O_2}$  values (calculated) between the NNO and HM oxygen buffers for petrographically pristine late-Quaternary minette lavas intimately associated spatially (and probably genetically) with leucite basanites in western Mexico. These values of temperature and  $f_{O_2}$  are in agreement with those under which phlogopite was crystallized in the high-pressure experiments.

Garnet peridotite xenoliths in the Navajo minettes called The Thumb and Ship Rock equilibrated at depths of ~110 km and at temperatures ranging from 950° to 1230°C (Ehrenberg, 1979, 1982), nearly the same conditions ( $T \cong 1150^\circ C$ ,  $P \cong 42$  kbar) obtained by Mercier (1976) for a diopside xenocryst in the Ship Rock minette. It is improbable that the Navajo minette magmas formed at shallower depths than the xenoliths they bear. As the xenoliths contain phlogopites that are chemically identical or very similar to minette micas, it is clear that, irrespective of whether there has been interaction between the xenoliths and minette magma, such micas can form in the upper mantle at temperatures as great as 1250°C and pressures of 40 kbar or more, conditions essentially equivalent to those under which ultrapotassic rocks and kimberlites originate.

The chemical identity of minette micas and many of the "secondary metasomatic" micas of kimberlites and man-

tle xenoliths indicates that metasomatism and consequent mantle heterogeneity are important factors in the origin of both minettes and kimberlites (but see Wyllie and Sekine, 1982, for an alternative explanation). On the basis of a large number of experimental and theoretical studies in recent years on peridotite- $H_2O$ - $CO_2$  systems, it appears that source-rock composition—as influenced by metasomatism, partial melting, and reaction between liquids and solids—as well as the absolute and relative abundances of  $H_2O$ ,  $CO_2$ , and halogens at the time of magma generation are decisive factors in determining whether the magma produced from a K-rich mantle source will be minette-like, kimberlitic, or ultrapotassic (see, e.g., Ryabchikov and Green, 1978; Baldrige *et al.*, 1981; Luhr and Carmichael, 1981).

The inter- and intra-grain chemical variations seen in minette micas are probably due to small-scale magmatic heterogeneities produced by mixing of batches of magma of similar but differing composition, as suggested by Smith *et al.*, (1978) and Mitchell and Meyer (1980), as well as high- and low-pressure evolution of minette magma.

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<sup>4</sup> Note, however, that Robert (1976) suggests that high-temperature—high-Ti phlogopites may be of either high- or low-pressure origin.

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#### Appendix—Source papers for mica analyses

(Full references are given only for those publications not cited in the list of references or earlier in this appendix. Sources are listed in alphabetical order within rock-type subdivisions).

A. In *Minettes*: Ehrenberg, 1979; Gallagher, 1963; Hall, 1982; Kramer, 1976; Luhr and Carmichael, 1981; Métais *et al.*, 1962; Némec, 1972; Nicholls, 1969; Roden and Smith, 1979; Scott, 1979; Velde, 1969; Velde, D., 1971, Les lamprophyres à feldspath alcalin et biotite: minettes et roches voisines. *Contributions to Mineralogy and Petrology*, 30, 216–239; Williams, H., 1936, Pliocene volcanoes of the Navajo-Hopi country. *Bulletin of the Geological Society of America*, 47, 111–172.

B. In *Kersantites and Other Lamprophyres* (other than minettes): Cooper, 1979; Grapes, 1975; Griffin and Taylor, 1975; Janse, 1977; Kramer, 1976; Leavy, B. D., and Hermes, O. D., 1979, Mantle xenoliths from southeastern New England. In F. R. Boyd and H. O. A. Meyer, Eds., *The Mantle Sample: Inclusions in Kimberlites and Other Volcanics*, p. 374–381. American Geophysical Union, Washington, D.C.; McHone, 1978; Métais *et al.*, 1962; Némec, 1972; Nicholls, 1969; Platt and Mitchell, 1982; Rimsaite, 1971; Rock, 1978; Rock, 1982; Strong and Harris, 1974; Velde, 1969;

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